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Supporting information

A Green Approach to the Synthesis of Ag Doped Nano Magnetic γ-Fe_2O_3@SiO_2-CD Core–Shell Hollow Sphere as an Efficient and Heterogeneous Catalyst for Ultrasonic-Assisted A^3 and KA^2 Coupling Reactions

S. Sadjadi*[a], M. Malmir,[b] M. M. Heravi*[b]

[a] *Gas Conversion Department, Faculty of Petrochemicals, Iran Polymer and Petrochemical Institute, PO Box 14975-112, Tehran, Iran. E-mail: samahesadjadi@yahoo.com*

[b] *Departmentof Chemistry, School of Science, Alzahra University, PO Box 1993891176, Vanak, Tehran, Iran Tel.: +98 21 88044051; fax: +98 21 88041344*

mmh1331@yahoo.com

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1. General information

The schematic processes of synthesis of the catalyst are depicted in Scheme 1. This catalyst was prepared from commercially inexpensive available materials and fully characterized using, the corresponding data, provided by FT-IR, SEM/EDX, XRD, TGA, BET, ICP-AES and VSM techniques.

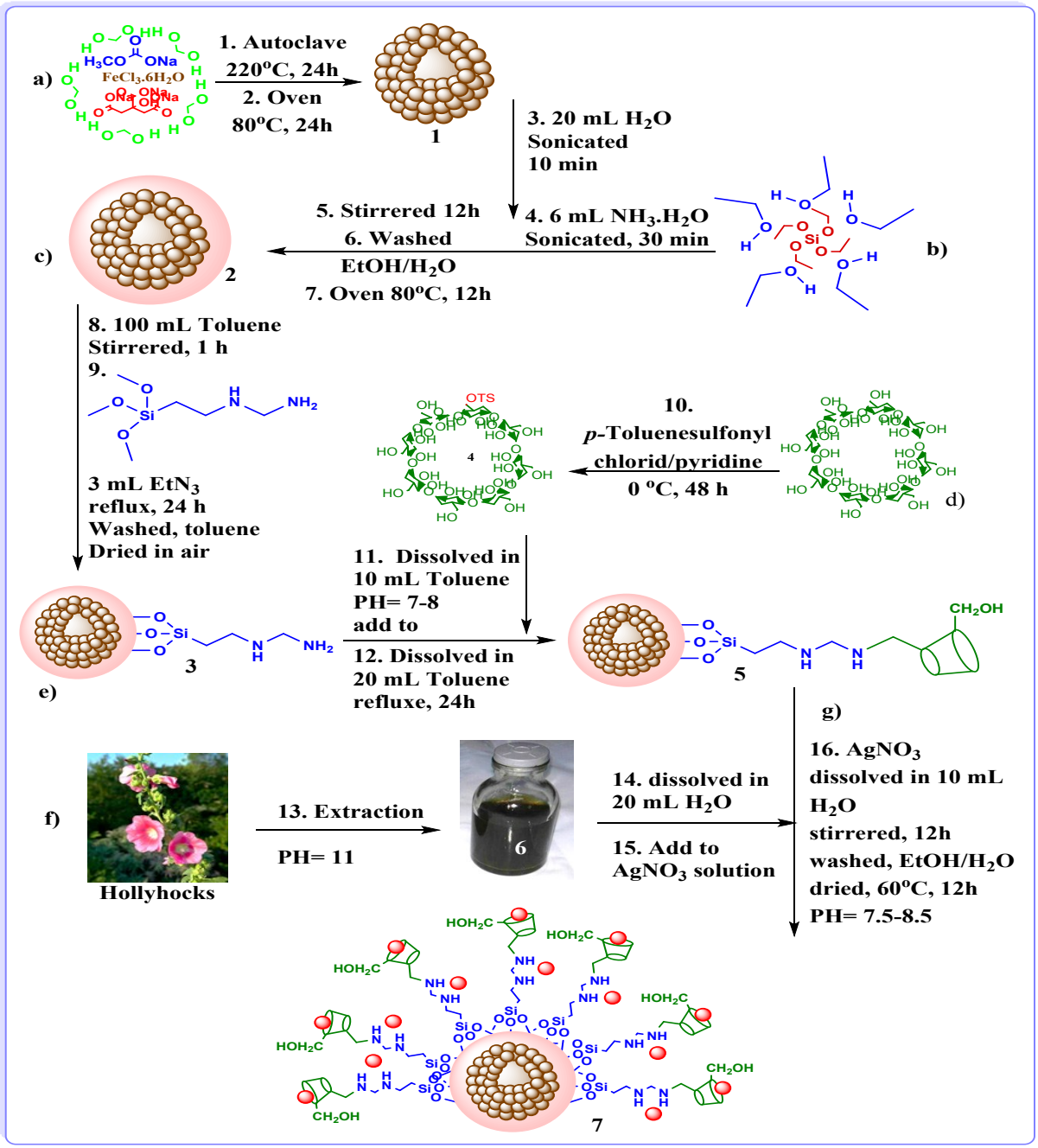
1.1. General details

All chemicals and reagents, including trisodium citrate dihydrate, sodium acetate trihydrate, $FeCl_3 \cdot 6H_2O$, TEOS, β-cyclodextrin, N-(2-(trimethoxysilyl)ethyl)methanediamine, toluene, triethylamine, acetone, ethanol, ethylene glycol (EG), urea, $AgNO_3$ and $NH_3 \cdot H_2O$, were analytical grade reagents, purchased from Sigma-Aldrich, and used without further purification. The progress of the organic reactions were monitored by TLC on commercial aluminum-backed plates of silica gel 60 F254, visualized, using ultraviolet light. Melting points were determined in open capillaries using an Electrothermal 9100 without further corrections. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DRX-400 spectrometer at 400 and 100 MHz respectively. The catalyst characterization was performed by using various characterization techniques including XRD, FTIR, BET, SEM/EDX, TGA, and ICP-AES. FTIR spectra were obtained by using PERKIN-ELMER- Spectrum 65 instrument. The BET analyses were carried out using BELSORP Mini II instrument. Prior to BET analyses, the samples were degassed at 423 K for 3h. SEM/EDX images were recorded by employing a Tescan instrument, using Au-coated samples and acceleration voltage of

20 kV. Room temperature powder X-ray diffraction patterns were obtained by using a Siemens, D5000.CuKα radiation from a sealed tube.

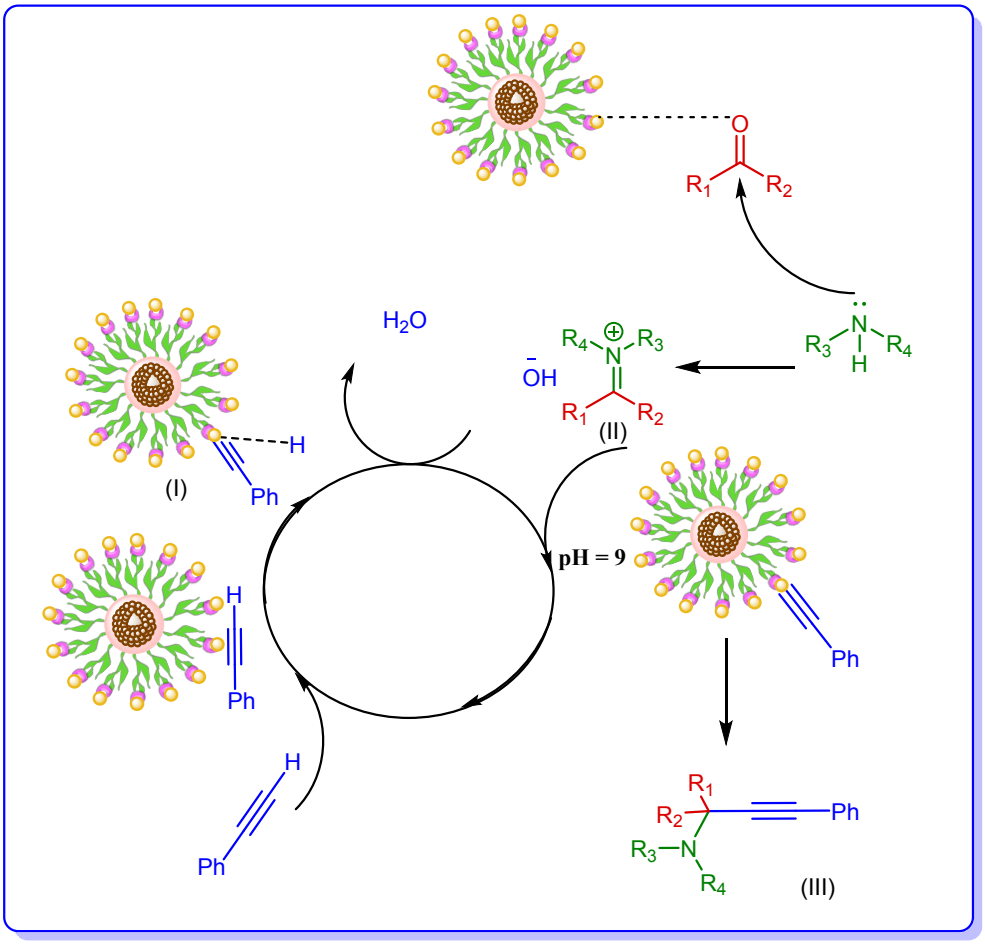
2. Characterizations of Catalyst

2.1. Possible formation process



Scheme 1 The possible formation process of h-Fe_2O_3@SiO_2-CD/Ag hollow spheres

2.2. Mechanism of the reaction



Scheme 2 Plausible mechanism for the synthesis of propargylamine by h-Fe_2O_3@SiO_2-CD/Ag.

2.3. FT-IR analysis

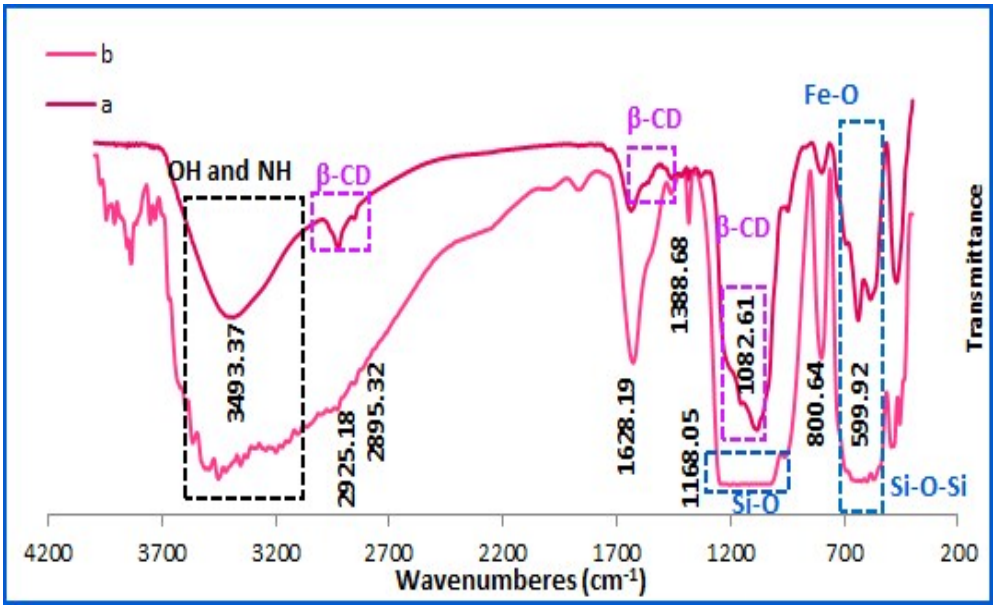


Fig. 1 The FT-IR spectra of a) h-Fe_2O_3@SiO_2-CD and b) h-Fe_2O_3@SiO_2-CD/Ag

2.4. X-ray diffraction spectra

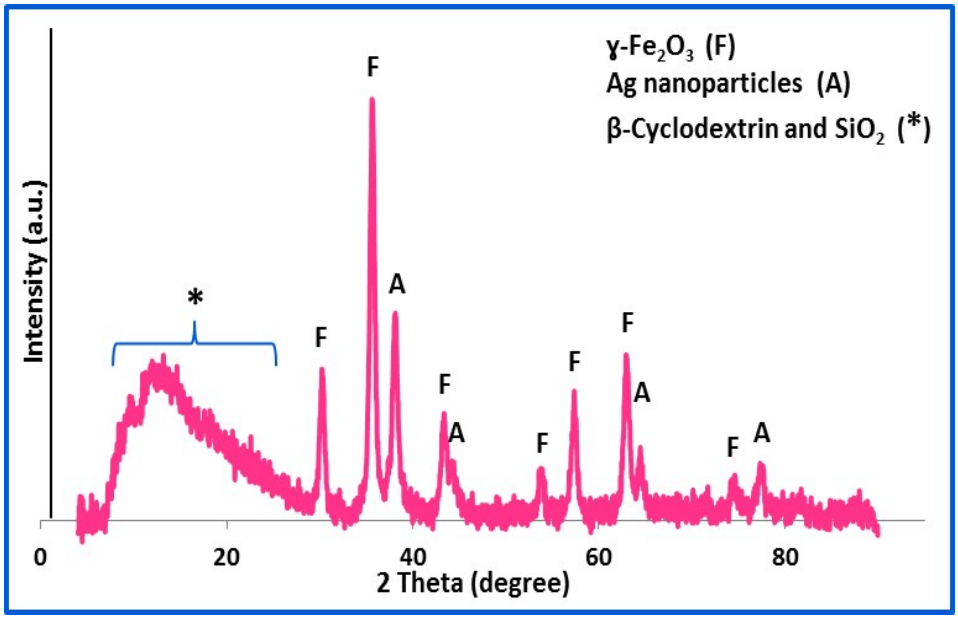


Fig. 2 The XRD pattern of h-Fe_2O_3@SiO_2-CD/Ag

2.5. TGA analysis

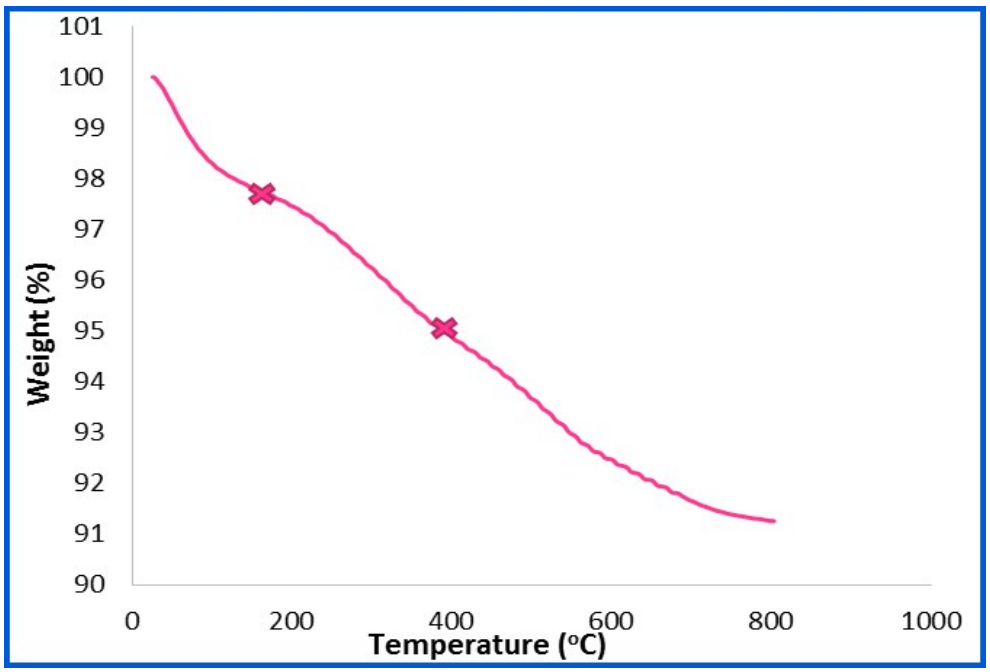


Fig. 3 The TGA analysis of the h-Fe_2O_3@SiO_2-CD/Ag

2.6. VSM analysis

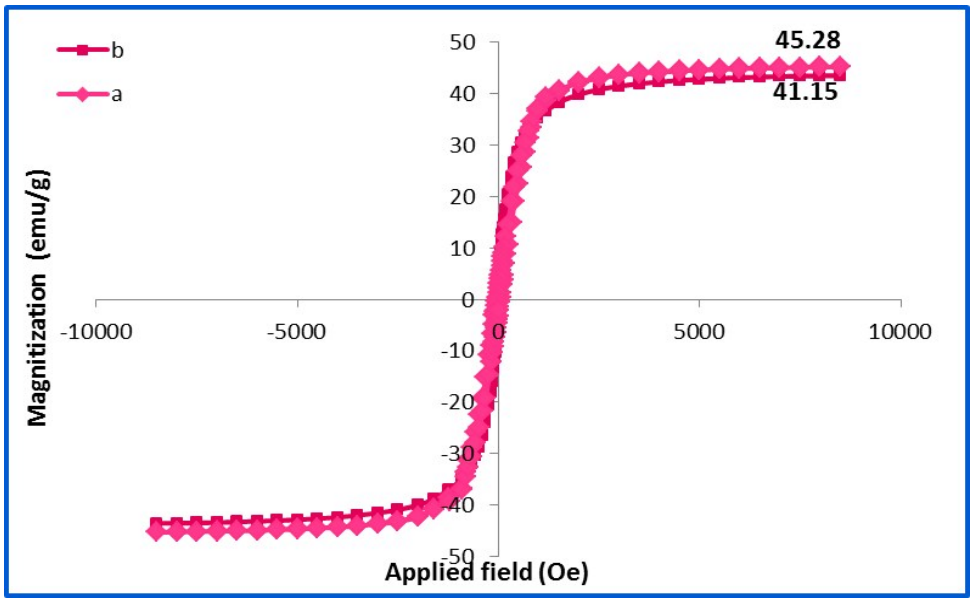


Fig. 4 VSM analyses of a) h-Fe_2O_3 and b) h-Fe_2O_3@SiO_2-CD/Ag

2.6. SEM/EDX analysis

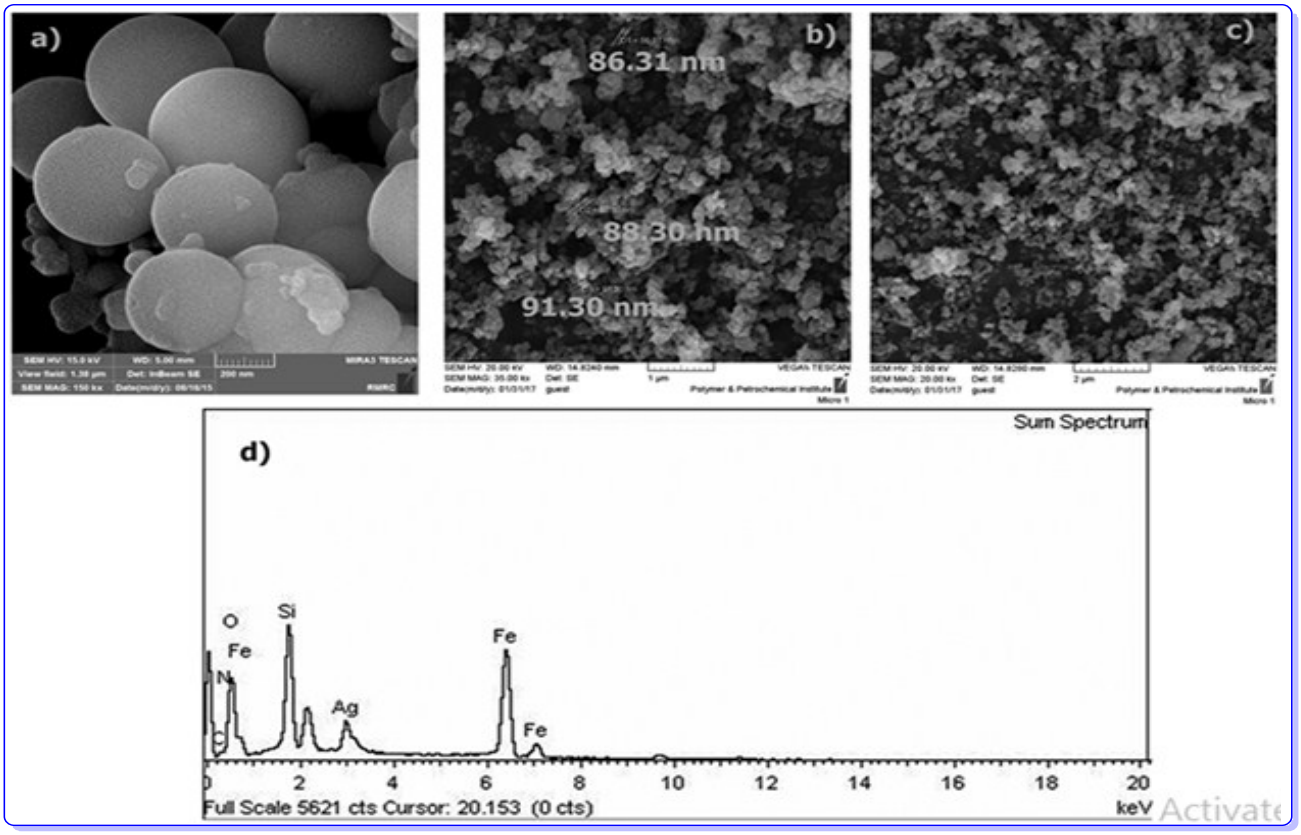


Fig. 5 The FE-SEM analysis of a) h-Fe_2O_3@SiO_2 and SEM analyses of b) h-Fe_2O_3@SiO_2-CD c)h-Fe_2O_3@SiO_2-CD/Ag and d) the EDX analysis of h-Fe_2O_3@SiO_2-CD/Ag

2.7.The elemental mapping image

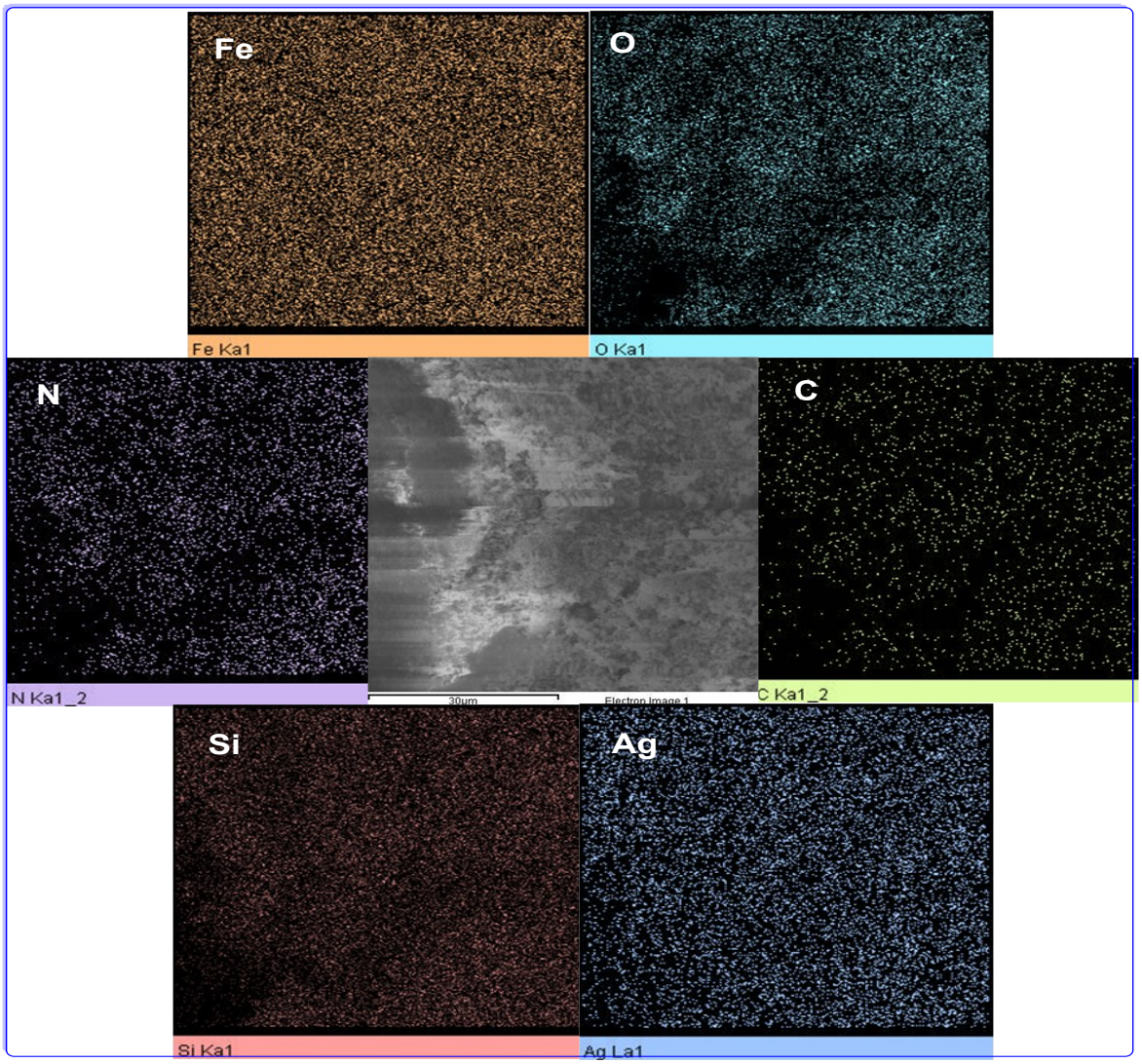


Fig. 6 The elemental mapping analysis of h-Fe_2O_3@SiO_2-CD/Ag

2.8. N_2 adsorbtion-desorbtion analysis

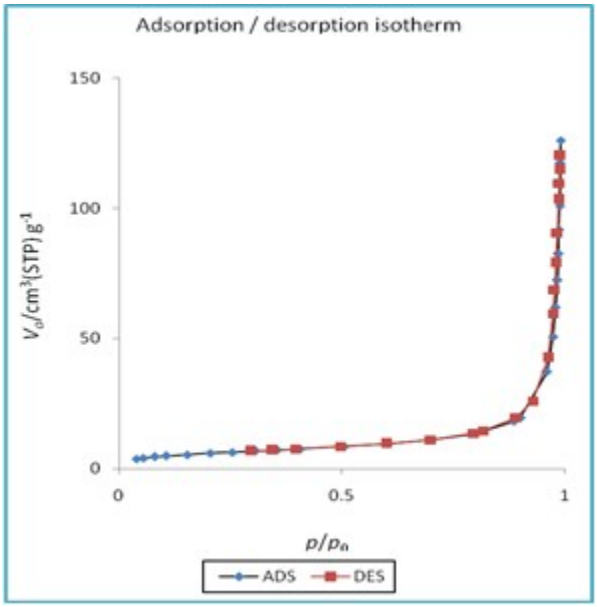
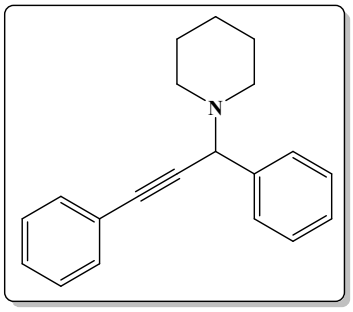
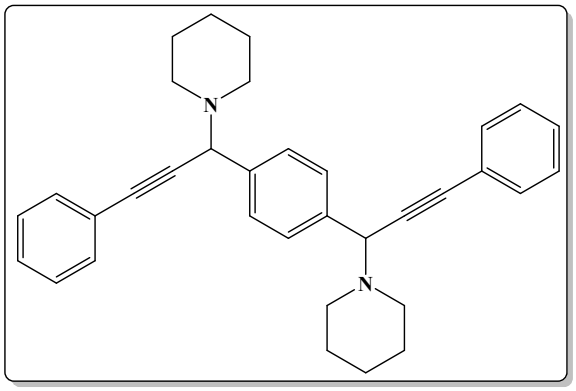


Fig. 7N_2 adsorption-desorption isotherms of the catalyst

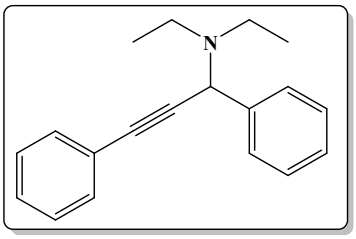
3. Spectral data for selected compounds[1]



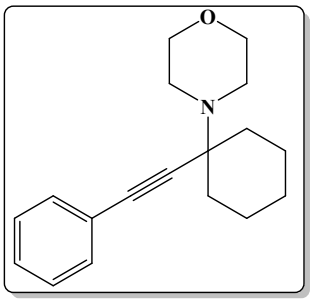
1-(1,3-diphenylprop-2-ynyl)piperidine (Table 2, 4a): Pale yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.45-1.49 (m, 2H), 1.58-1.65 (m, 4H), 2.59 (t, 4H), 4.81 (s, 1H), 7.31-7.40 (m, 6H), 7.53-7.55 (m, 2H), 7.65-67 (d, J=7.6 Hz, 2H).



1-(3-phenyl-1-(4-(3-phenyl-1-(piperidin-1-yl)prop-2-ynyl)phenyl)prop-2-ynyl)piperidine(Table 2, 4h): White solid; mp 157-159 ^{o}C (Lit.[1] 158-160 ^{o}C); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.47 (m, 2H), 1.59-1.63 (m, 4H), 2.59 (m, 4H), 4.81 (s, 1H), 7.33-7.35 (m, 3H), 7.52-7.55 (m, 2H), 7.63 (s, 2H).



N,N-diethyl-1,3-diphenylprop-2-yn-1-amine(Table 2, 4q): Pale yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.04 (m, 6H), 2.36-2.62 (m, 4H), 5.19 (s, 1H), 7.15-7.27 (m, 4H), 7.29-7.38 (m, 3H), 7.39-7.41 (m, 2H).



4-(1-(2-phenylethynyl)cyclohexyl)morpholine(Table 2, 4s): Pale yellow oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 1.28-1.30 (m, 1H), 1.52 (m, 2H), 1.63-1.67 (m, 3H), 1.73 (br.s, 2H), 2.03-2.05 (m, 2H), 2.74 (br.s, 4H), 3.78 (br.s, 4H), 7.27 (m, 3H), 7.44-7.45 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 22.7, 25.7, 35.4, 46.6, 58.8, 67.4, 86.4, 89.8, 123.4, 127.7, 128.1, 131.7.

3.1. Copies of ^{1}H and ^{13}C NMR for selected products [1]

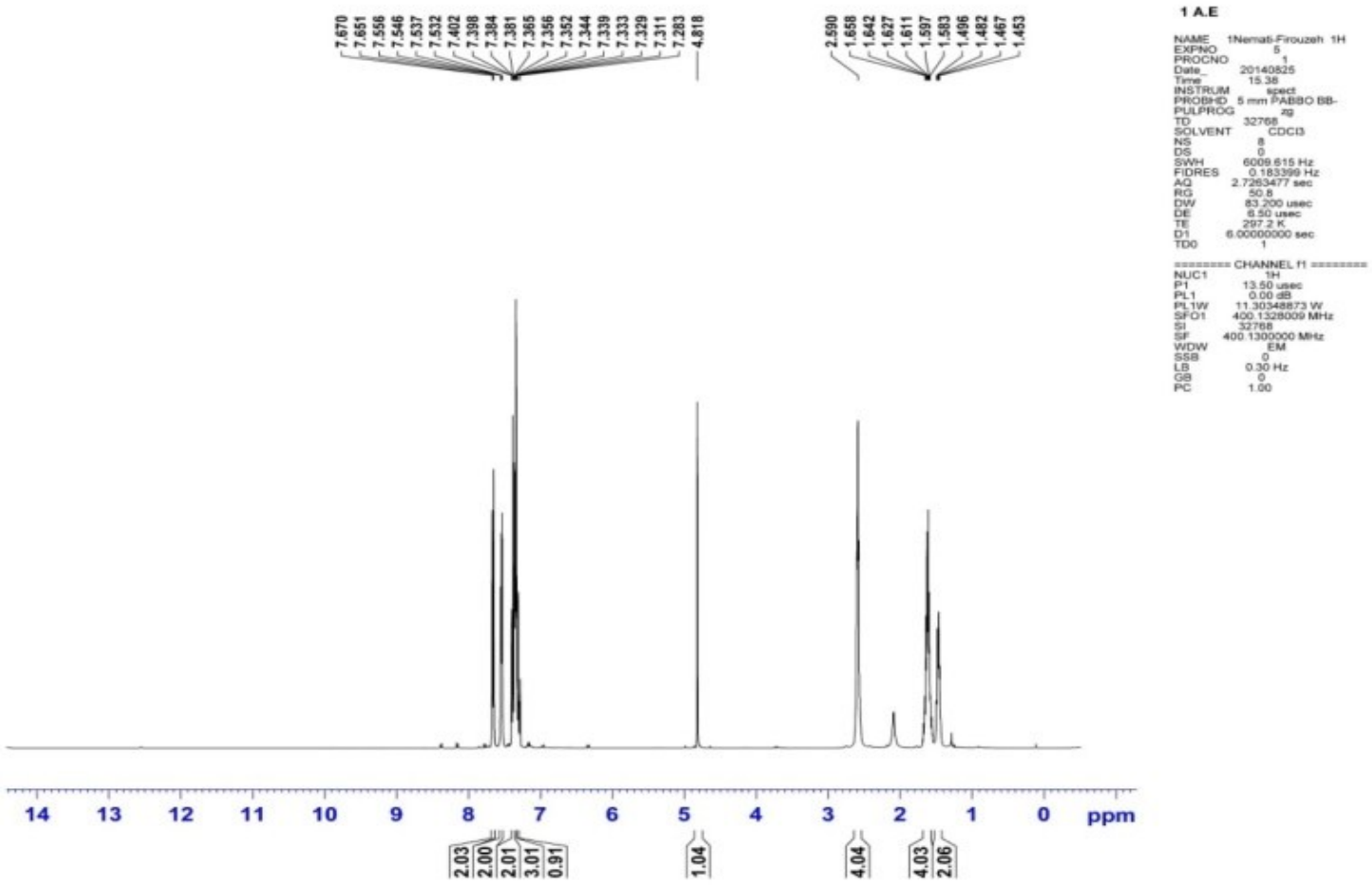
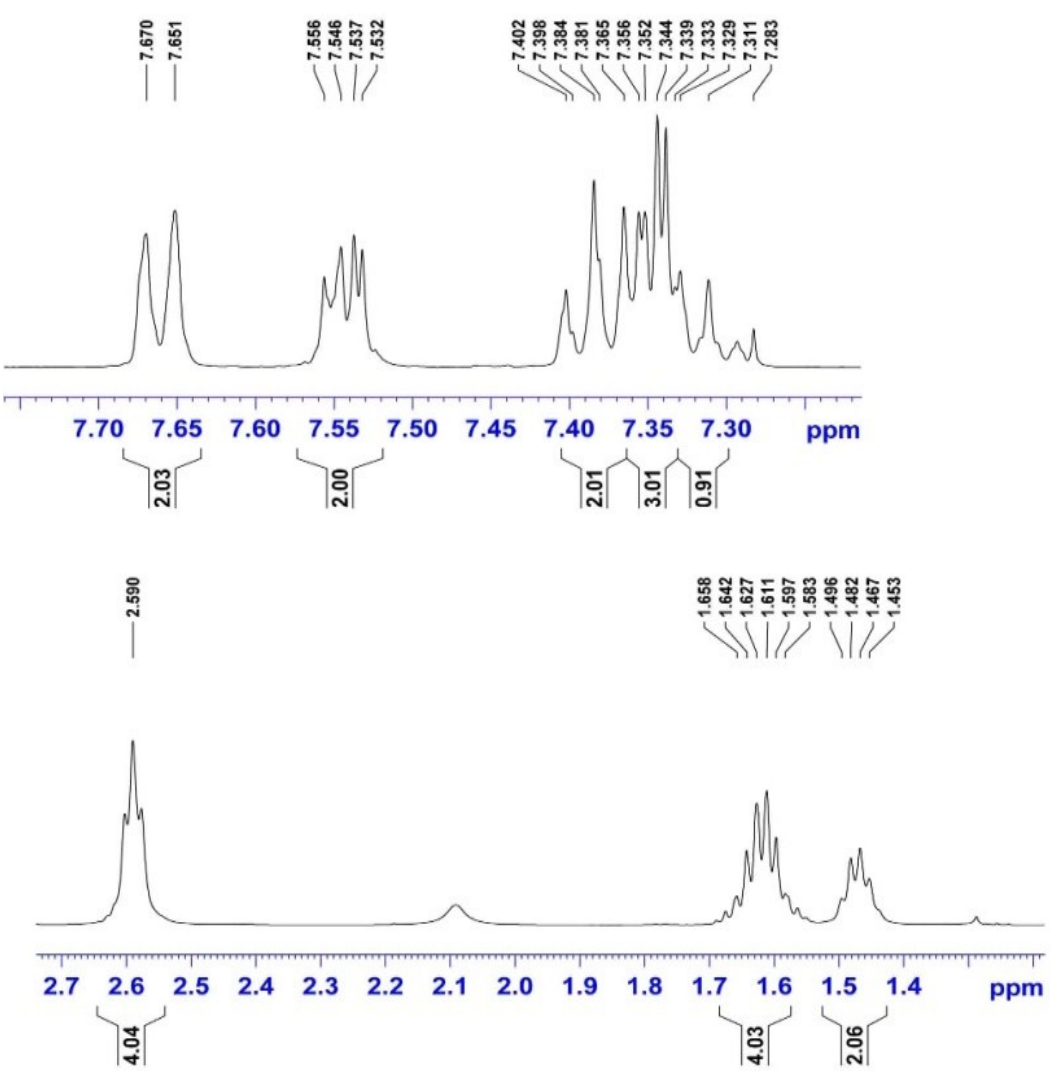


Fig. 8 ^{1}H NMR spectrum of **(Table 2, 4a)**



1 A.E

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PROCNO 1
Date_ 20140825
Time 15.38
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TD 32768
SOLVENT CDCl3
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DS 0
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FIDRES 0.183399 Hz
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RG 50.8
DW 83.200 usec
DE 6.50 usec
TE 297.2 K
D1 6.00000000 sec
TD0 1

======== CHANNEL f1 ========
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SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig. 9 [1]H NMR, Expand spectrum of **(Table 2, 4a)**

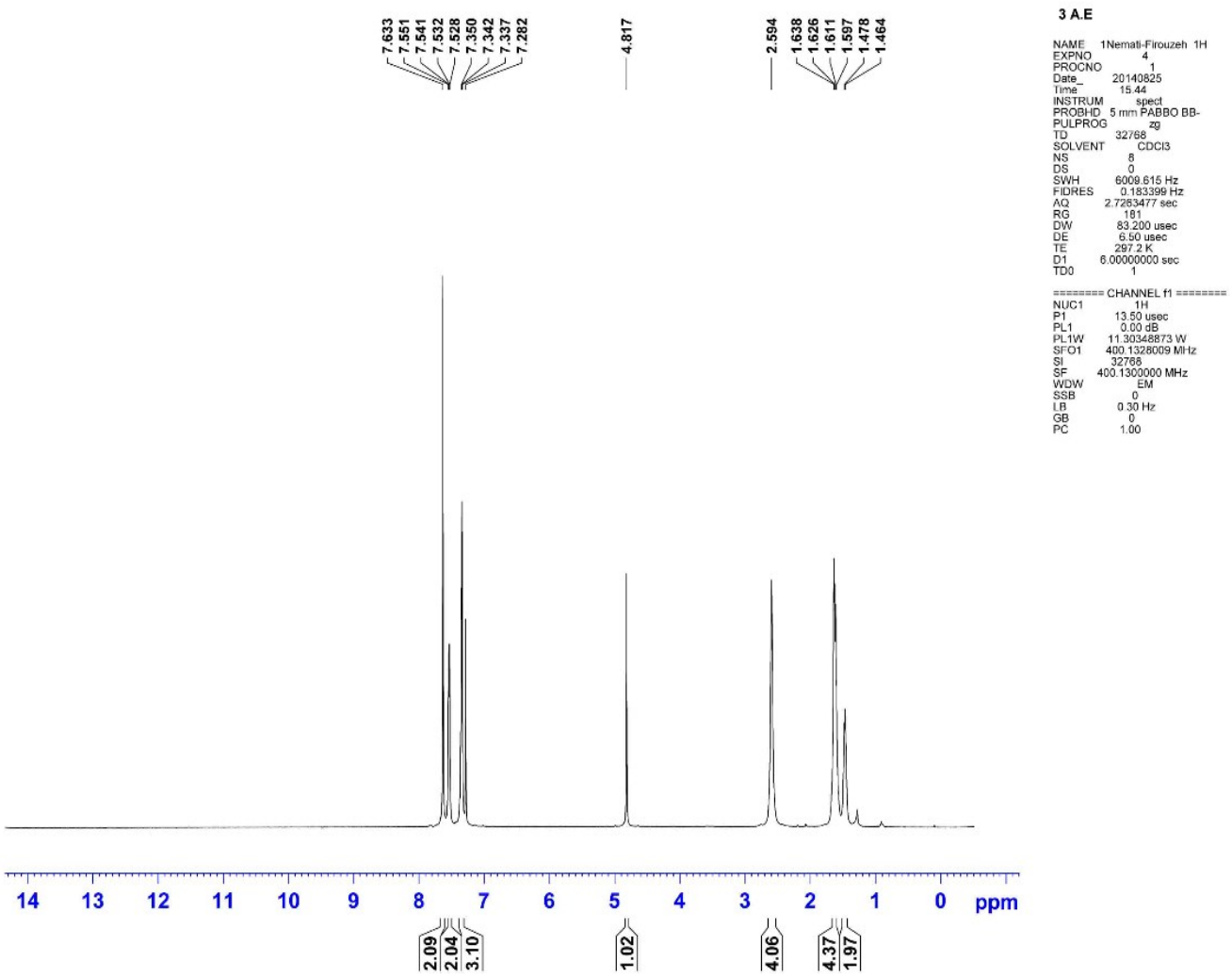
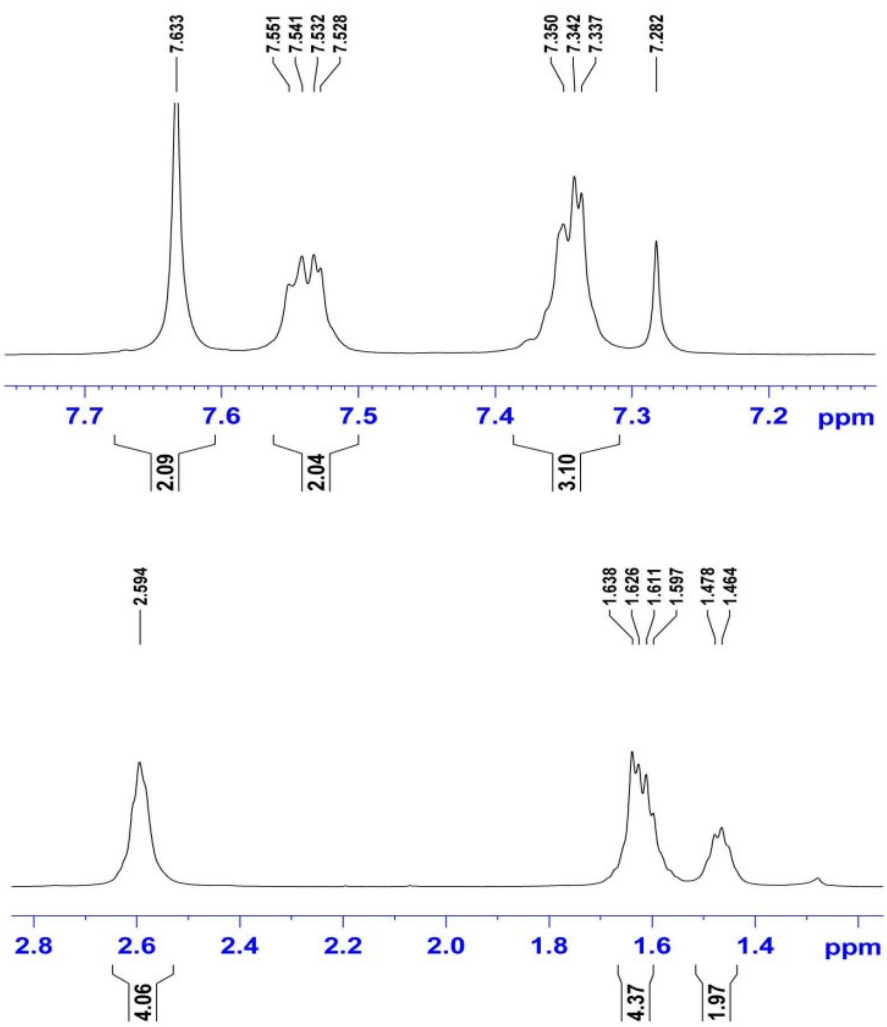


Fig. 10 ^{1}H NMR, spectrum of **(Table 2, 4h)**



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TD 32768
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SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7263477 sec
RG 181
DW 83.200 usec
DE 6.50 usec
TE 297.2 K
D1 6.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 0.00 dB
PL1W 11.30348873 W
SFO1 400.1328009 MHz
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig.11 ^{1}H NMR, Expand spectrum of **(Table 2, 4h)**

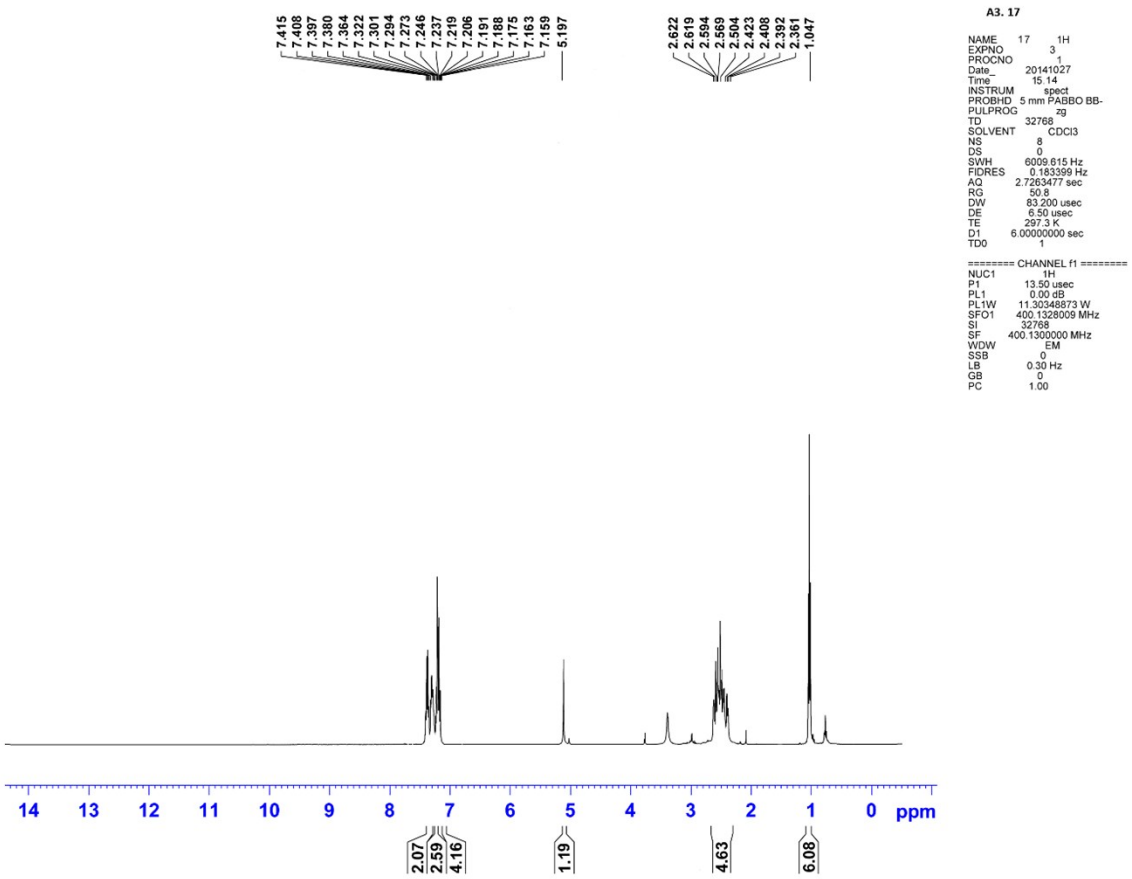

Fig. 12 ^{1}H NMR, spectrum of **(Table 2, 4q)**

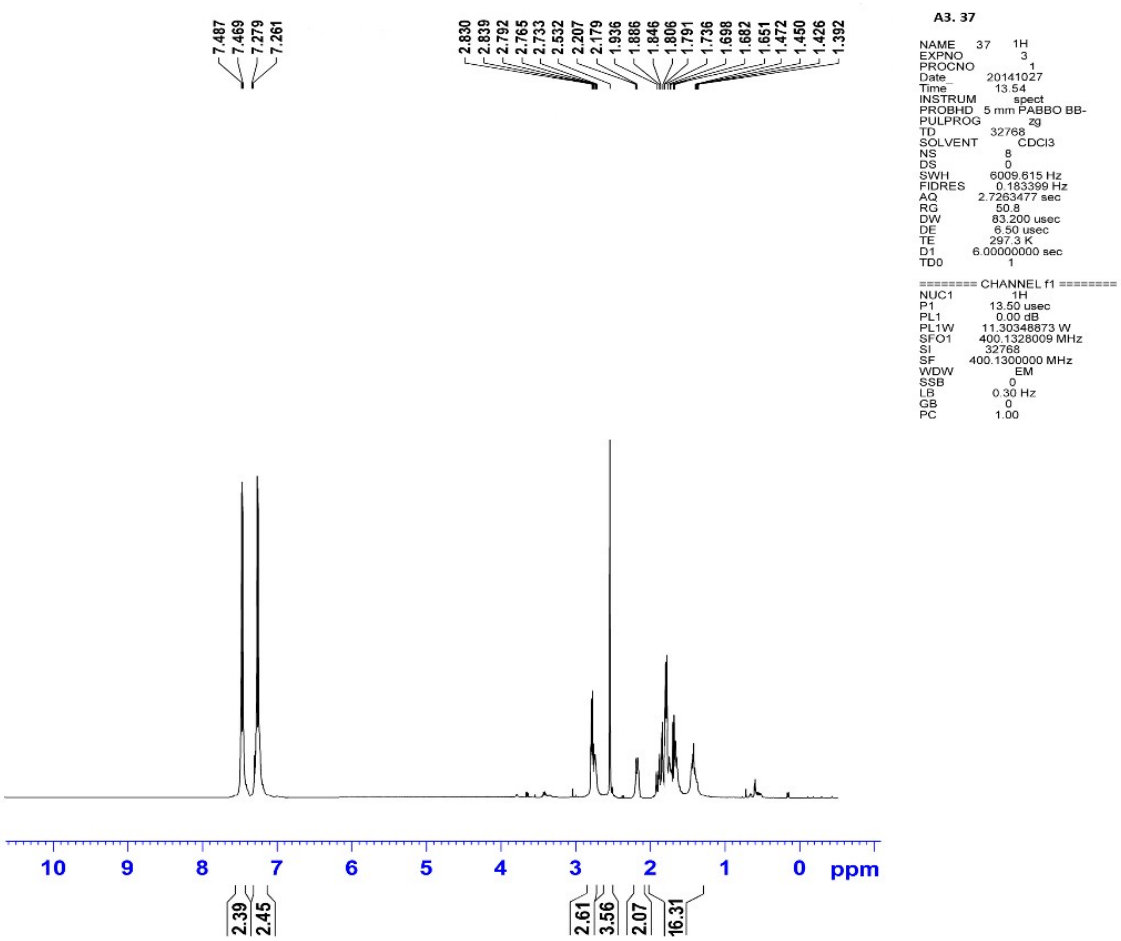

Fig.13 ^{1}H NMR, spectrum of **(Table 2, 4s)**

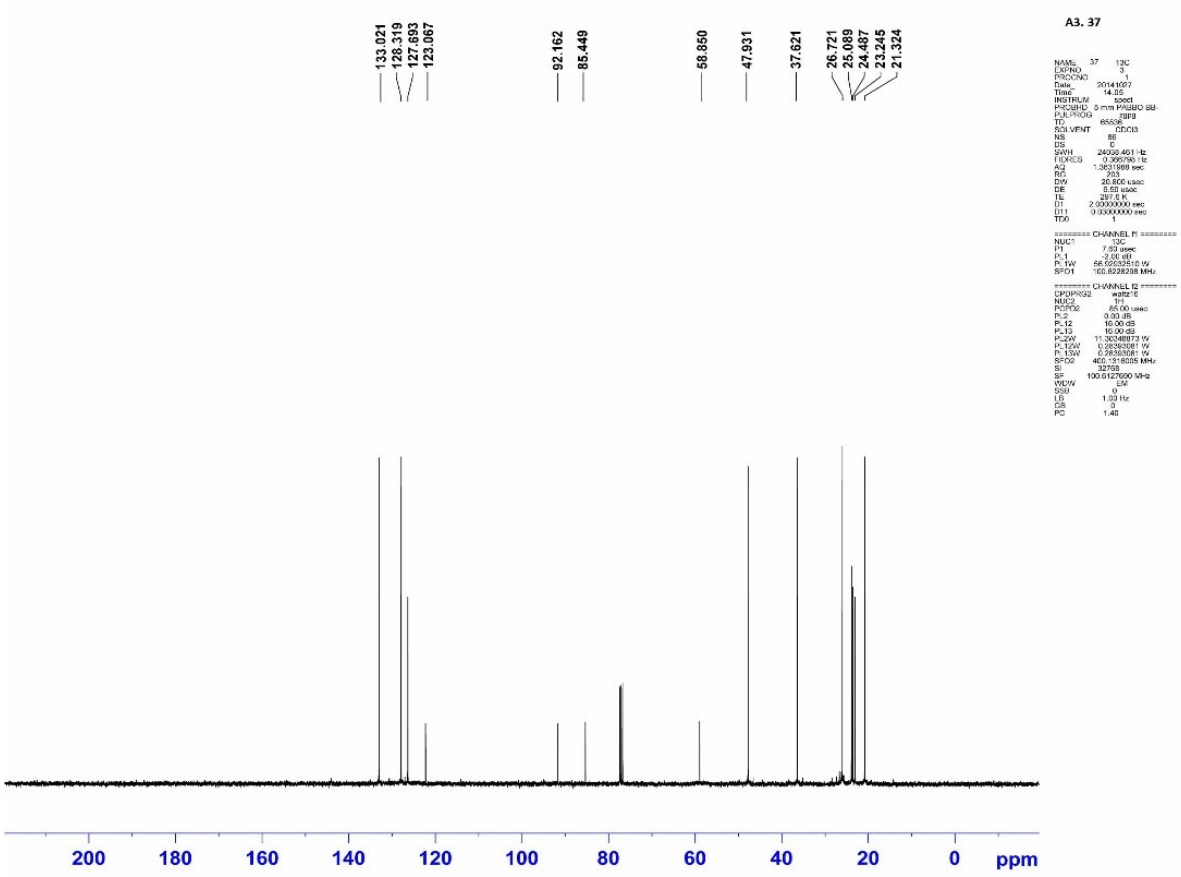

Fig.14 ^{13}C NMR, spectrum of **(Table 2, 4s)**

Reference:

[1] A. Elhampour, M. Malmir, E. Kowsari, F. A. Boorboor and F. Nemati, *RSC Adv.*, 2016, **6**, 96623-96634.